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A search for effective diffusion barriers for semiconductor metallization systems that was carried out under this contract and can be conveniently classified in two categories: diffusion barriers that are thermodynamically stable with respect to reactions with the underlying substrate and the overlying metal film, and diffusion barriers that are thermodynamically unstable with respect to these adjacent media. Two contacting systems have been used as prototypes: silicon with an aluminum metallization, and GaAs with Ag or Au metallization. This report contains the results of this effort.

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CHARACTERIZATION OF DIFFUSION BARRIERS FOR METALLIZATION SYSTEMS

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The search for effective diffusion barriers for semiconductor metallization systems that was carried out under this contract can be conveniently classified in two categories: diffusion barriers that are thermodynamically stable with respect to reactions with the underlying substrate and the overlying metal film, and diffusion barriers that are thermodynamically unstable with respect to these adjacent media. Two contacting systems have been used as prototypes: silicon with an aluminum metallization. and GaAs with Ag or Au metallization.

Only the Si/Al contact system was considered in the search for a thermodynamically stable diffusion barrier. Little progress was accomplished along that line. One reason is that both Si and Al are metallurgically quite reactive elements. This fact narrowly limits the number of acceptable materials. Of all materials we have investigated under this contract, only VB_2 qualifies as a compound that may be stable in contact with Si or Al. (The experimental evidence at hand is consistent with thermodynamic stability, but insufficient to prove it.) Another reason for the slow progress is the limited effort we spent on the search for a thermodynamically stable compound. There are no fundamental reasons why a good and thermodynamically stable diffusion barrier should not exists for the Si/Al metallization system. But what this diffusion barrier should be remains an open question.

Much has been accomplished in developing good diffusion barrier schemes with thermodynamically unstable materials. At the start of the contract, one of the best diffusion barriers available was a reactively sputtered TiN. For the Si/Al contact system, failure temperatures of TiN barriers are in the range of 550°C or less for a 30 min heat treatment.

Our investigations have covered four distinct types of barriers. They are listed in the table below in ascending order of effectiveness for the Si/Al contact system, as measured by the two monitoring techniques of RBS (which senses atomic instabilities) and reverse saturation current of shallow pn junctions (which senses electrical instabilities of the contact). The TiN barrier is included in the table for reference.

Amorphous transistion metal alloys fare poorly compared to TiN. The reason is that they typically contain an early and a late transition metal and that the former tends to react strongly with Al, while the latter readily reacts with Si. We believe that good amorphous diffusion barriers can be found, but they will have to come from a different class of amorphous metallic alloys. The subject deserves further study.

Tungsten nitride deposited by reactive sputtering is superior to reactively sputtered TiN. This finding is a major result of our research. The sputtering conditions are less critical for W_xN_{1-x} than they are for TiN which constitutes another practical advantage of the W_xN_{1-x} barrier. On the basis of our findings, we predict a promising future for applications of tungsten nitride diffusion barriers.

Our most outstanding results have been recorded with reactively sputtered conducting oxides. The three oxides we have tested so far are all excellent even though they are dissimilar in their chemical properties and in their mechanism of conduction. Their common property is that they are all thermodynamically unstable in contact with Al. Cross-sectional transmission electron micrographs indeed confirm that a very thin layer develops upon annealing at the interface between Al and the oxides. The seflsealing nature of this reaction must be a reason for the excellent results. It is too early to conclude that oxides are useful as diffusion barriers in the Al/Si contact because the forward characteristic of pn junctions does show a degradation for the same treatment that leaves the reverse saturation current unchanged. The reason is under investigation, but it is probably that the interfacial aluminum oxide layer becomes too thick for tunneling to accomodate the current. The subject is clearly one that needs to be pursued, because the stability recorded with oxide barriers for reverse-biased junctions is truly outstanding.

Barrier Type	Implementation	Failure Temperature (°C) (after 30 min ammealing) RBS	Saturation Current
amorphous transistion metal alloys	$W_{70}Zr_{30}$	500	500
	$W_{40}Zr_{60}$	500	500
interstitial alloys	TiN	550	500
	$W_{75}C_{25}$	500	
	VB_2	550	550
	$W_{80}N_{20}$	600	600
	$W_{60}N_{40}$	600	600
oxides	$Mo_{80}O_{20}$	550	>600
	RuO_2	>650	
	In_2O_3	>600	>650

Ohmic contacts to both p- and n-type GaAs have been studied with diffusion barriers of interstitial alloys and conducting oxides. All cases yield far superior stability than the conventional GaAs/Ni-Ge-Au contacting scheme that does not contain a diffusion barrier. The latter one fails after 10 min at 450°C. All the contact systems that we tested withstood 550°C for 30 min at least (GaAs substrate with TiN/Ag), or 60 min and longer (GaAs substrate with $W_{60}N_{40}$/Ag or $Mo_{80}O_{20}$/Al or Ni-Ge/$W_{60}N_{40}$/Au). Among these, only the Ni-Ge/$W_{60}N_{40}$/Au contacting scheme had a contact resistivity that is comparable with the 10^{-6} Ohmcm^2 of the conventional alloyed Ni-Ge-Au scheme. The problem that needs to be addressed with GaAs contacting schemes is therefore that of developing suitable contacting layers. Once this is accomplished, we believe that it should be possible to borrow much of what has already been learned regarding diffusion barriers on silicon contacts and design reliable metallization schemes for GaAs that much surpass the alloyed contact now commonly used.

Because of the potential practical significance we foresee for tungsten nitride and conducting oxide thin films, we have established in detail how the sputtering conditions affect the deposition and the film. We discovered in the process that the materials fall in two clearly distinct groups; RuO_2 (and TiN) on one side, and W_xN_{1-x} (and Mo_xO_{1-x}) on the other. The reasons are not well understood. Considering the importance of sputtering as a deposition process for thin films in general, this observation suggests new directions of very relevant investigations.

The following individuals have participated in the activities of this contract under full or partial support or as collaborators:

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Two PhD Theses were completed during the course of this contract:
Hannu Kattelus, June 3, 1988: "Diffusion Barriers in Semiconductor Contact Metallizations"
Frank C.T. So, July 31, 1988: "Diffusion Barriers for VLSI Applications"

The papers published with acknowledgements to this ARO contract are listed in the appendix.

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